and R. C. Sherwood for making measurements on our samples.

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Crystal Structure of Bullvalene at 25°[1]

Sir:

The self-interconversion of bullvalene has been studied by nmr in solution,[2] where it was found that at 120° all protons are magnetically indistinguishable, while at −85° the spectrum corresponds to that for a single valence tautomer. A solid-state nmr investigation of bullvalene indicated that the line width decreases with increase of temperature above 0°.[3] This effect was interpreted[3] either as indicating reorientation about a molecular axis or as valence tautomerism occurring in the crystal. Crystal structure analyses on two bullvalene–AgBF$_4$ complexes[4,5] have provided evidence for only a small amount of valence tautomerism occurring in these solid complexes. The Ag$^+$ ions complex to several double bonds and the resulting "freezing" of these bonds in definite positions reduces the number of self-rearrangement pathways. We have investigated the crystal structure of bullvalene itself at 25 ± 3° to determine whether there are unique positions for the bullvalene molecules in the crystal at this temperature and to investigate the extent of valence tautomerism in the solid.

Bullvalene (C$_{10}$H$_{10}$) crystallizes as transparent plates belonging to the monoclinic system. The most obvious choice of unit cell is virtually orthogonal (β' = 90° 20'), but this cell does not correspond to a conventional description for any space group. A simple transformation of reciprocal and real lattice axes leads to the following cell dimensions (Mo Kα, λ 0.7107 Å) at 25°: a = 6.21 ± 0.03, b = 20.73 ± 0.05, and c = 10.52 ± 0.04 Å; and β = 148° 18' ± 30'. The transformed cell belongs to the space group P2$_1$/c, with four molecules of C$_{10}$H$_{10}$ in the unit cell. Intensity data were obtained by equiinclination Weissenberg photographs and visual estimates. A total of 988 independent structure amplitudes was obtained. The crystal structure was solved by the symbolic addition technique,[6,7] and at the present stage of refinement, the crystallographic R factor is 0.14 on 988 reflections.

A view of the crystal structure looking down the b axis is shown in Figure 1. The packing is highly efficient and the definition of individual atoms indicates that motion of an entire bullvalene molecule about a molecular axis is not an important facet of the structure at this temperature. The agreement among the dimen-
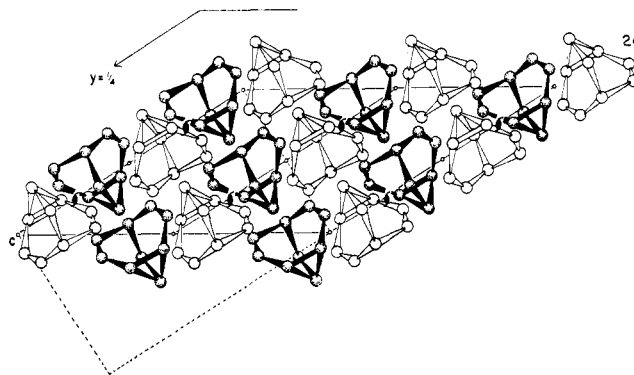

Figure 1. A view of the contents of two unit cells looking down the b axis. The bonds in the bullvalene molecules above $y = \frac{1}{2}$ are shaded in black. In this projection, one of the atoms in the three-membered ring completely obscures another atom in one-half of the molecules and is completely obscured by that atom in the other half. The a' and c' axes of the pseudo-orthogonal cell are marked by discontinuous lines at the lower portion of the drawing.

sions of chemically equivalent features within the bullvalene molecule is in accord with the estimated standard deviations (C–C distance ±0.02 Å, C–C–C angles ±1°). The mean C=C, C(sp^2)—C(apex), C(sp^2)—C(three-membered ring), and C—C (within the three-membered ring) distances are 1.33, 1.51, 1.45, and 1.54 Å, respectively. The angles at the apical carbon atom are close to tetrahedral, and those at the carbon atoms participating in the double bonds are all significantly greater than 120° (mean 126°); the average internal angle in the three-membered ring is 60° and the average external angle at the three-membered ring is 122°. There are no anomalous features in a three-dimensional difference map to indicate unusual atom vibrations, and indeed, well-defined positions can be found for most hydrogen atoms.

We conclude that the packing forces prevent substantial valence tautomerism from occurring in the bullvalene crystal at 25°. The rearrangement observed in the 3:1 bullvalene–AgBF$_4$ complex[4] must be due to less restrictive packing forces in that crystal.[7a]

(7a) NOTE ADDED IN PROOF. An electron diffraction study of bullvalene vapor reveals molecular dimensions in very good agreement with those found in the X-ray analysis: B. Andersen and A. Marstrander, *Acta Chem. Scand.*, 21, 1676 (1967).
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Topography of Nucleic Acid Helices in Solutions. V. The Interactions of L-, D-, and DL-Amino Acid Derivatives with Nucleic Acid Helices. Demonstration of an Asymmetric Surface[1]

Sir:

We wish to report the synthesis and the interactions of several amino acid amides of the general structure I,

(1) For part IV in this series see E. J. Gabbay and R. R. Shimshak, *Biopolymers*, in press.

(1) Work supported by U. S. Public Health Service Grant GM 12470-03.
(2) R. Merenyi, J. F. M. Oth, and G. Schröder, *Chem. Ber.*, 97, 3150 (1964).
(3) J. D. Graham and E. R. Santee, Jr., *J. Am. Chem. Soc.*, 88, 3453 (1966).
(4) M. G. Newton and I. C. Paul, *ibid.*, 88, 3161 (1966); J. S. McKechnie, M. G. Newton, and I. C. Paul, *ibid.*, 89, 4819 (1967).
(5) J. S. McKechnie and I. C. Paul, *Chem. Commun.*, in press.
(6) An authoritative review of this method is given by J. Karle and I. L. Karle, *Acta Cryst.*, 21, 849 (1966).
(7) Full details will be published at a later date.